

MULTIFUNCTIONAL STRUCTURAL COMPOSITE BATTERIES FOR U.S. ARMY APPLICATIONS

J.F. Snyder*, D.M. Baechle, and E.D. Wetzel

U. S. Army Research Laboratory, Weapons and Materials Research Directorate
Aberdeen Proving Ground, MD 21005

K. Xu

U. S. Army Research Laboratory, Sensors and Electron Devices Directorate
Adelphi, MD 20783

ABSTRACT

We are developing structural polymeric composites with battery functionality. These devices carry structural loads while simultaneously storing electrochemical energy. If designed with sufficient structural and energy efficiency, these materials could enable significant system-level weight reductions by replacing inert structural components while providing supplementary power for light load applications. To enable this concept, we have designed mechanical load-bearing properties directly into the battery electrodes and electrolyte such that each component is itself multifunctional. Carbon fiber fabric anodes, structural cathodes, and solvent-free structural polymer electrolytes are each being developed to exhibit a desirable combination of mechanical strength and electrochemical performance. These components are being integrated using moldable, scalable, cost-effective composite processing techniques. A case study using a real system is reviewed to demonstrate potential benefit.

1. INTRODUCTION

The weight and volume of conventional energy storage technologies greatly limits the performance of a range of U.S. Army platforms, including soldier systems, ground vehicles, and unmanned vehicles. Significant research efforts are currently underway to reduce battery weight and volume through improvements in battery efficiency. A different approach is to design batteries that are also load-bearing (Snyder et al., 2006). These multifunctional structural batteries could be used to replace conventional structural components, such as vehicle frame elements or a UAV wing structure, with components capable of storing energy. If designed with sufficient structural and energy efficiency, these structural batteries could enable significant system-level weight reductions (Thomas and Qidwai, 2004).

Previous examples of structural batteries have primarily utilized structural packaging. (Qidwai et al., 2005). The current study instead explores a multifunctional composite battery concept that utilizes a fiber-matrix composite platform in which each structural component is designed to function as an electrochemical

battery component. The basic design (Fig 1) consists of a carbon fiber fabric acting as an anode, a porous insulating separator layer, an electrically conductive structural substrate (e.g. metal mesh, carbon fabric) coated with a cathode material, and a structural solid polymer electrolyte binding the components together. A lithium-based chemistry has been chosen due to its high energy density and compatibility with polymer-based electrolytes (Xu, 2004). The electrodes both carry mechanical load while storing electrochemical energy. The insulating separator layer provides additional structural support while ensuring electrical isolation of the electrode layers. The polymer-based electrolyte transfers load to the other components and simultaneously conducts ions between electrodes. Each component is fulfilling multiple roles in the composite device, allowing for a synergistic weight or volume reduction to be accomplished compared to the individual state-of-the-art (SOA) battery and structure. The challenge of this design, however, is to create components that fulfill their multiple roles simultaneously and cooperatively.

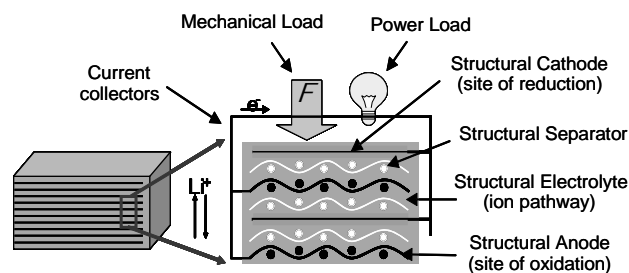


Figure 1. Concept for a structural battery.

This paper will discuss recent development and optimization of the each of the components of the structural lithium-ion battery: the anode, cathode, and electrolyte materials. Each component is designed to provide multifunctionality of both structural and electrochemical properties. The fabrication approach used to combine these components into an integrated structural battery composite is then described. Initial efforts to develop a structural supercapacitor, which is similar in design to the battery, are also reviewed.

Report Documentation Page				Form Approved OMB No. 0704-0188	
Public reporting burden for the collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to a penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.					
1. REPORT DATE DEC 2008		2. REPORT TYPE N/A		3. DATES COVERED -	
4. TITLE AND SUBTITLE Multifunctional Structural Composite Batteries For U.S. Army Applications				5a. CONTRACT NUMBER	
				5b. GRANT NUMBER	
				5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S)				5d. PROJECT NUMBER	
				5e. TASK NUMBER	
				5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) U. S. Army Research Laboratory, Weapons and Materials Research Directorate Aberdeen Proving Ground, MD 21005				8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)				10. SPONSOR/MONITOR'S ACRONYM(S)	
				11. SPONSOR/MONITOR'S REPORT NUMBER(S)	
12. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release, distribution unlimited					
13. SUPPLEMENTARY NOTES See also ADM002187. Proceedings of the Army Science Conference (26th) Held in Orlando, Florida on 1-4 December 2008					
14. ABSTRACT					
15. SUBJECT TERMS					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT UU	18. NUMBER OF PAGES 8	19a. NAME OF RESPONSIBLE PERSON
a. REPORT unclassified	b. ABSTRACT unclassified	c. THIS PAGE unclassified			

Special emphasis is placed on selecting scalable composites manufacturing routes. Preliminary data pertaining to the properties of the whole composite battery are also discussed. The paper concludes with a case study describing the potential benefit through application to an unmanned ground vehicle.

2. ELECTRODE DESIGN AND CHARACTERIZATION

2.1 Anode

Our current structural battery design uses conventional carbon fiber fabrics as an anode material. Carbon fibers are inherently multifunctional in a manner well-suited for this application. Carbon fibers can serve as the media for the intercalation of lithium ions for lithium-based battery chemistries. (Takami et al., 2001) Their continuous structure and inherent electrical conductivity obviate the need for a polymer binder and metal substrate that add parasitic mass in more traditional granular carbon anodes. Carbon fibers have a high stiffness and strength which provides mechanical reinforcement for the composite battery. In addition, they are cost-effective, scalable materials that are often fabricated specifically for composite applications.

The electrochemical properties of carbon fibers and their usefulness in battery applications are complex and dependent on the fiber composition. The properties of commercial fibers are particularly absent in the literature, even though these materials present the most efficient means to rapid scale-up of new fiber-based technologies. We have therefore studied a wide range of fiber types and grades to rapidly identify those of interest (Wong et al., 2008); we have also studied the fiber morphologies and intercalation mechanisms (Snyder et al., submitted). This research further enables us to better understand how commercial fibers compare to standard anodes as well as high performing fiber-based anodes that have been developed on the laboratory-scale.

Several forms of structural carbon were evaluated in this research, including woven and nonwoven fabrics employing fibers based on polyacrylonitrile (PAN) and pitch precursors. Fabrics based on activated carbon, carbon nanotubes, and carbon nanofoams were also evaluated. PAN-based fibers under study were T300 (Toray Industries Inc), AS4 and IM7 (Hexcel Corp.), PX30 and PX35 (Zoltek Corp.), and T40/800 (Cytac Industries Corp.). PAN-based nonwoven fabrics with chopped fibers were obtained from Hollingsworth and Vose Corp. in grades 80000-15, -20, -28, -30, -33, -36, -37, -39, and -47 which pertain to thicknesses ranging from 0.05mm to 0.84mm. Pitch-based carbon fibers were provided by Nippon Graphite Fibers (NGF) Corp., in grades YSH70A and YSH50A (high modulus, high compressive strength), YS80A and YS95A (ultra high

modulus, high thermal conductivity), and CN90 and CN60 (high modulus, commercial grade), and XN15 and XN05 (low modulus, commercial grade).

Morphologies of several representative pitch- and PAN-based fibers were studied using Raman spectroscopy. Spectra were taken using a 532nm laser on a LABRam ARAMIS spectrometer (HORIBA Jobin Yvon, Inc) at 50x magnification under ambient conditions. The cross-section of each fiber was evaluated to gauge the characteristics of the entire fiber, and the area of measurement was approximately the area of an average fiber cross-section. The spectra baselines were corrected for fluorescence and Savitsky-Golay smoothing was applied to minimize photon spikes.

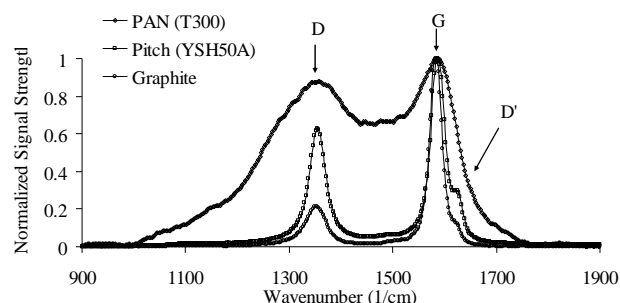


Figure 2. Raman spectra for representative carbon fibers

Figure 2 presents representative Raman spectra for a PAN-based fiber (T300), high modulus pitch-based fiber (YSH50A), and graphite. The graphs have each been normalized by the highest point to facilitate comparison. The D and D' modes, occurring here around 1350 cm^{-1} and 1625 cm^{-1} , correspond to disorder in the carbon regions. Peak broadening indicates increased concentrations of amorphous carbon for the PAN-based fibers relative to graphite and the pitch-based fibers. (Ferrari et al., 2000). The G mode, occurring here around 1590 cm^{-1} , corresponds to in-plane bond-stretching of sp^2 carbon atoms and is the more dominant mode in polycrystalline graphite. The ratio of the respective peak intensities of the D and G modes relates to the amount of disorder in the graphitic regions, which is often correlated with lithium capacity. It is visibly apparent that the granular graphite has the greatest order, followed by the pitch-based fibers and PAN-based fibers respectively. This is expected since pitch-based fibers are typically more graphitized than PAN-based fibers. Anodes that incorporate chopped pitch-based fibers often support higher electrochemical capacities during cycling.

The electrochemical properties of each of the electrode materials were characterized on a Maccor 4000 battery test system using a 15mm coin cell configuration. Carbon electrodes were made by cutting 10mm disks out of the fabrics. Lithium foil was used as the counterelectrode and separated from the carbon fabric by

a polypropylene separator. The cell was immersed in a liquid electrolyte composed of 1.0 M LiPF₆ in EC/DMC (30:70). The half-cell battery cycling was run at a constant current of 1.2×10^{-4} A over the first two cycles to ensure proper formation of the solid electrolyte interphase (SEI). The SEI results from electrolyte solvents reductively decomposing on carbonaceous anodes during the first cycle. If well formed it can prevent further decomposition and enable stable, reversible device performance (Fong et al., 1990); otherwise it can lead to high internal resistances or cell failure. The current was increased to 4.0×10^{-4} A for the remainder of the test. Tests were run for approximately 50 cycles. Most samples were run in triplicate and the results averaged.

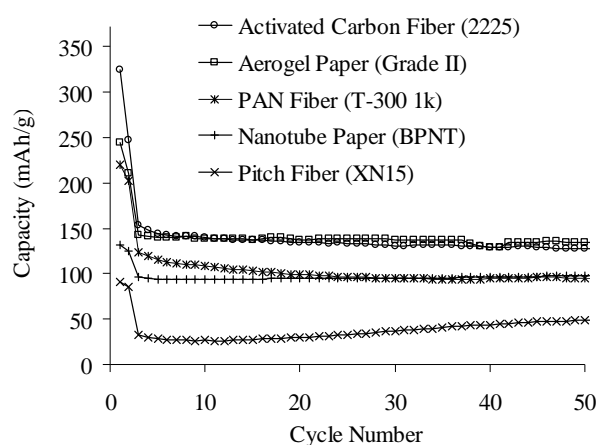


Figure 3. Specific capacity for several carbon fiber and fabric materials that have been cycled vs. lithium foil

Figure 3 illustrates the cycle performance for samples from a high performing grade in each fiber/fabric category. The initial drop in capacity occurs during SEI formation. The subsequent plateau exhibited relatively little loss. The decline in capacity over the first two cycles accounted for at least 95% of the capacity loss over the life of the experiment for most samples. PAN-based fibers significantly outperformed the pitch-based fibers, which is surprising considering that pitch-based materials are typically more valued for battery applications given their higher graphite concentration as affirmed by Figure 2. One possible explanation is that the graphitic layers in PAN-based fibers may be more accessible to lithium ions or more amenable to SEI formation. The pitch and PAN-based fibers contain both graphitic sheets and a disordered carbon core, and the lithium insertion mechanisms of these morphologically-hybridized systems are still not well understood. Much of the capacity, as well as the capacity loss, may be a function of the fiber geometry and diameter. It is possible that the larger disordered carbon cores in PAN-based fibers more efficiently augment the reversible capability for ion uptake.

One concern with commercial fibers is the interference between fiber sizing and cycling of the electrolyte constituents. Sizing is composed of uncured epoxy resin and applied to the fiber surface to facilitate handling and to increase fiber-matrix interactions. Commercial graphitic fibers are typically not available without the sizing. To evaluate the impact of sizing, several of the fibers were de-sized by solvent extraction and tested. De-sizing did not appear to improve electrochemical capacity or the cyclability. The removal of the sizing might also harm the surface of the fiber in a small, but critical, manner. Our structural batteries will therefore use fibers as received regardless of sizing.

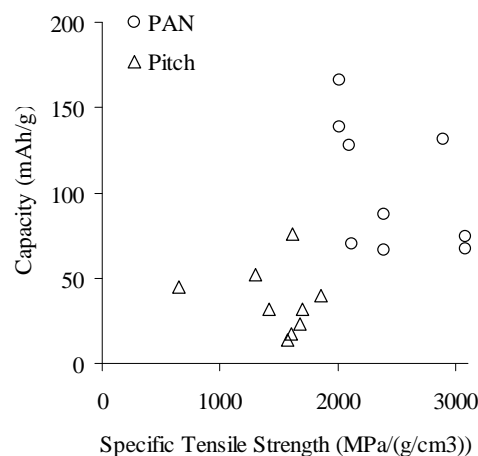


Figure 4. Multifunctional properties of carbon fibers relating capacity at the 3rd cycle (vs. lithium foil) to specific tensile strength.

Figure 4 correlates electrochemical performance with a critical structural property, tensile strength. Materials exhibiting desirable performance in both properties will lie in the upper right quadrant of the graph. There is considerable scatter to the data in Figure 4, but capacity appears to generally increase with increasing specific tensile strength. Overall trends clearly indicate PAN-based fibers to provide superior multifunctional behavior according to these metrics. Our studies show T300 to possess the most desirable combination of energy storage (160 mAh/g after 50 cycles; practical areal density of at least 3.0 mAh/cm² anticipated in a working cell) and mechanical properties (3.5 GPa tensile strength, 230 GPa tensile modulus). It should be noted that these analyses are an initial assessment and the standalone fiber properties are less critical than performance in a composite. In addition, the current study does not reflect the impact of electrochemical cycling on fiber mechanics, or the impact of tensile load on lithium intercalation. These experiments are currently underway.

2.2 Cathode

The multifunctional cathodes must be electrically conductive and structurally robust. To achieve this, a laminate design similar to commercial cathodes has been employed in which a primary electrical bus (current collector) is coated with a cathode film. However, in this work the electrical bus is designed to be load-bearing and to enable matrix interpenetration. Porous metal foils and carbon fabrics are both under consideration. The precise film composition and processing route are optimized for high electrochemical capacity, electrical conductivity, rechargeability, and mechanical integrity.

Lithium Iron Phosphate (LiFePO_4) is used as the active intercalation material that provides electrochemical capacity. Commercially supplied LiFePO_4 (Phostech Industries) was combined with an electrically conductive additive and milled to reduce particle size to increase bulk electrical conductivity. The conductive additive is necessary for facilitating electron transport between the cathode particles and the current collector. Acetylene black, a form of carbon powder with high conductivity, is most frequently used as the conductive additive. After milling, the powder was combined with poly(vinylidene fluoride) (PVDF) binding agent in a mixed solvent system. The suspension was applied to the substrate and hot pressed at up to 200 °C and 900 kg of pressure.

The exact formulation of LiFePO_4 , acetylene black and polymer binder, as well milling procedure and hot press conditions are all interdependent variables. Electrochemical capacity is provided only by the LiFePO_4 , which is used in as high a concentration as possible. However, its high resistivity requires not only the conductive additive but also milling to break down the particle sizes and create a well-dispersed mixture. The milling results in small particle sizes that require even more acetylene black to properly percolate the electrical network, and enough polymer to properly bind the mixture. Compression in the hot press helped form a better, denser film with higher conductivities.

The cathode half cells were run in a similar configuration as the anodes at a constant current of 9×10^{-5} A for the first two cycles while the SEI layer formed, and at 3×10^{-4} A for the remainder of the test. A capacity fade between the first and third cycles was found to be much less than that of the anodes, and it was about 20% for most configurations. After the third cycle the specific capacity was usually found to plateau until the test was terminated. Tests were run for about 50 cycles.

It was found that 18% acetylene black in 82% LiFePO_4 , milled for 3 hours in an attritor mill followed by 24 hours in a horizontal ball mill, and cast in 17% PVdF, yielded the lowest resistivity and the highest

capacity values. Hot pressing this film on a T300 carbon fabric at 150°C and 900 kg pressure yielded a structural cathode with minimal cracking and resilient against dissolving in the electrolyte-matrix.

3. STRUCTURAL ELECTROLYTE SYNTHESIS AND CHARACTERIZATION

The structural electrolytes are designed to carry and transfer loads while maintaining adequate ion conductivity. These objectives are being engaged through progressive development of electrolytes based on load bearing ion conductive resins, nanocomposites of those resins, and “gels” composed of resins and liquid electrolytes. Battery power and structural modulus both benefit through the use of electrolytes based on processable resins that perform well as thin films. Minimizing the electrolyte thickness allows for higher battery current by limiting the distance ions must travel between electrodes. Minimizing the volume fraction of the electrolyte matrix also allows for a greater volume fraction of structural electrode materials, permitting the development of higher capacity, higher strength structural composite batteries.

To characterize the electrolyte resins, disks 1 cm in diameter and 0.5 mm thick were measured using electrochemical impedance spectroscopy and mechanical compression. These two properties are quick, useful metrics applicable for screening purposes. The results are most effectively plotted on multifunctional axes of conductivity vs. compressive modulus. Impedance measurements were performed using a Solartron 1260 Impedance Analyzer and Solartron 1287 Electrochemical Interface across a frequency range of 106 Hz to 10 Hz at room temperature (18 - 20 °C). Compression was performed in an MTS load frame employing a 5 kN load cell and a cross-head speed of 1 mm/min. The reported modulus values are calculated from the initial, relatively elastic portion of material loading curves. Downselected materials were studied in more depth.

In our initial work, a broad selection of monomers were complexed with lithium salts and thermally cured as solvent-free polymers. Varying the proportions, architecture, and functionalities of the monomers permitted for a wide range of tailorable structural and electrolytic properties. The results, which have been described in detail elsewhere (Snyder et al., 2007), are shown as open circles in Figure 5 and indicate a consistent tradeoff between structural and transport properties as the nature of the monomer is modified, with no strongly multifunctional outliers demonstrating uncommonly high properties.

Further investigation entailed copolymerizing pairs of monomers in order to study polymeric systems with

mixed architectures (Snyder et al., 2006). While monomer reformulation in homopolymers had not been effective at improving multifunctionality, copolymers of these same monomers did yield simultaneous improvements in ion conductivity and compressive modulus as seen in Figure 5. The copolymers allowed for a separation in function such that ion transport and stiffness were optimized through different monomers and not the same monomer. The gains in performance were not large, but they were striking in their consistency. The best efficiencies were found by matching the monomer that supported the highest ion conductivity with each of the monomers that provided the highest modulus values. This critical result broadly suggests that multifunctionality may be optimized by developing multicomponent systems in which each component is optimized for a specific function.

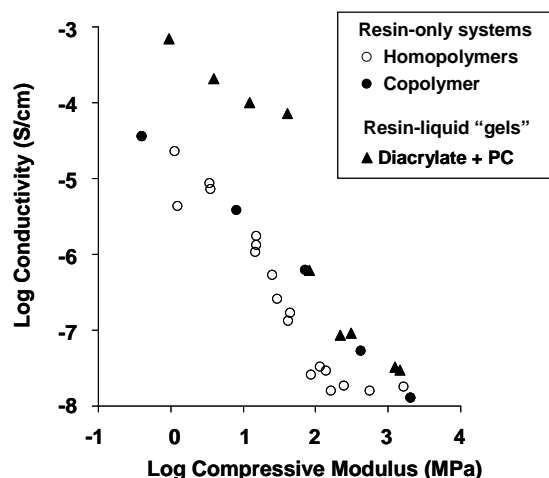


Figure 5. Room temperature ion conductivity vs. stiffness for resin-based gel structural electrolytes.

In recent work, the conductive component has been optimized by replacing the ion-conductive resin with liquid electrolytes. Studies have been performed using vinyl ester resins as well as epoxy-based resins. The former allows for facile resin injection and a wide range of architectures while the latter provides the ability to generate partially cured components (a.k.a. pre-pregs) that can be assembled and fully cured at a later time. The liquid-resin gels were formulated with 11 evenly dispersed formulations (100% liquid electrolyte, 90% liquid,...100 % crosslinking resin). Significant improvements in multifunctional performance of over an order of magnitude were realized by exchanging the ion conductive resin for a liquid electrolyte. Of note is the apparent drop in vinyl ester based gel performance (Fig. 5, solid triangles) at about 60 wt% liquid. Conductivity was undetectable below 50 wt% liquid in epoxy-based gels. These trends may correspond to a percolation mechanism whereby the liquid must sufficiently interpenetrate the system to provide high conductivity. The vinyl ester system is conductive along the entire

formulation curve since it is inherently conductive and also more likely to interact favorably with the polar liquids enabling solvent distribution.

In addition to the choice of resin, gel processing conditions and choice of solvent were also explored. Low temperature cure procedures were found to be beneficial as heating the samples caused some solvent evaporation and skewing of the data. Little difference was seen between solvents other than their inherent conductivity. Overall it has been found that a structural matrix can be formulated with high ion conductivity. Further work will employ the principles learned so far to develop more complex and efficient systems using both nanoparticles and liquid electrolytes in a resin framework, as well as controlled architectures to more efficiently utilize the structural and conductive regions.

4. BATTERY COMPOSITE FABRICATION AND CHARACTERIZATION

4.1 Processing

Vacuum assisted resin transfer molding (VARTM) was used as a processing route for our composite structural batteries. Using a VARTM approach minimizes void content, enables higher fiber volume fractions than simple hand-layup techniques, and is a highly scalable manufacturing route. The liquid resin monomer electrolytes as described in section 3 have been engineered to have sufficiently low viscosity such that they are amenable to VARTM processing. Our anode, cathode, and separator materials are also permeable and wettable, and are therefore compatible with traditional composite processes.

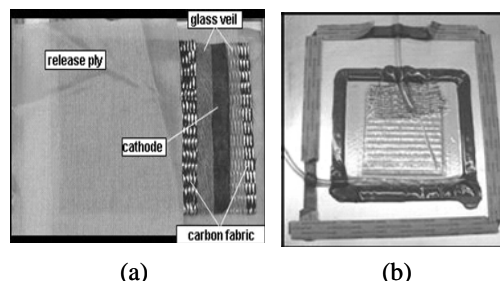


Figure 6. (a) Structural battery layers and (b) undergoing VARTM processing.

Figure 6 illustrates the fabrication of a typical composite battery. Between carbon fabric-based anodes and a thin film-coated, metal mesh cathode are 0.18-mm-thick glass veil separators (Grade 8000100, Hollingsworth and Vose). Using this separator allows compaction of the preform and high fiber volume fraction, while ensuring complete electrical insulation between the anode and cathode. A release ply and distribution media layer are then placed on top of the composite stack, and the preform is vacuum-bagged and

ported for resin inflow and outflow. The resin is pulled from a reservoir through the inflow port, wetting out the composite part, through suction provided at the outlet port. The part is then cured at 80°C in an oven overnight.

The preform example in Figure 6 is a symmetric, double-cell design. Note that this same approach can be easily scaled to many more cells and increasing cell areas, simply by changing the size and number of material layers. Integrated electrical bussing (not shown in this example) can also provide a means of creating series or parallel cell voltage arrangements, allowing for tailoring of the voltage and current capabilities of the cell. In addition, this VARTM technique is adaptable to complex part shapes and geometries through the use of contoured release plates, custom-geometry preforms, and carefully designed multi-port resin injection and venting schemes.

4.2 Supercapacitor Performance

Multifunctional supercapacitors have been developed with the two-fold purpose of being a testbed for generic device integration and laying the groundwork for high-performance structural supercapacitors. Supercapacitors, also known as electrochemical capacitors, operate by storing electrical charge along the double layer interface at each electrode. High surface area electrodes optimize this effect, such as carbon foams and nanotubes. Liquid electrolytes similar to those used in lithium batteries are used to transfer charge between electrodes.

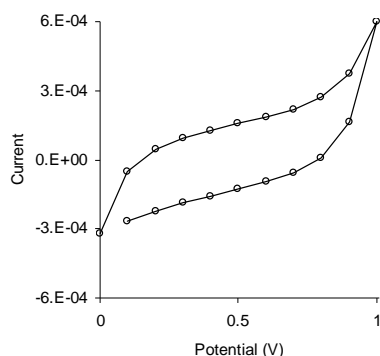


Figure 7. Cyclic voltammetry demonstrating charge-discharge performance of a structural supercapacitor after 30 cycles

Our layup consisted of a similar setup as described in section 4.1 for the structural battery, using gel electrolytes, however carbon fabrics were used as both electrodes and there is no battery cathode present. As Figure 7 illustrates, this cell demonstrated cyclable performance. The relatively low capacitance is attributed to the inherently low surface areas typical for commercial carbon fibers. Performance may be optimized by simply replacing these electrodes with higher surface area fabrics, such as have been demonstrated elsewhere (Qian 2008). Mechanical tests

are currently underway on several layup compositions to quantitatively determine the impact of liquid electrolyte concentration on mechanical performance.

4.3 Structural Battery

Composite batteries such as the ones shown in Figure 6 have shown basic electrochemical charging and discharging cycles. Full quantitative electrochemical performance characterization is in progress, and will be reported in a future publication.

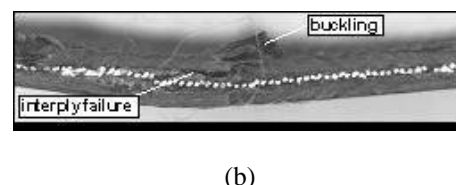
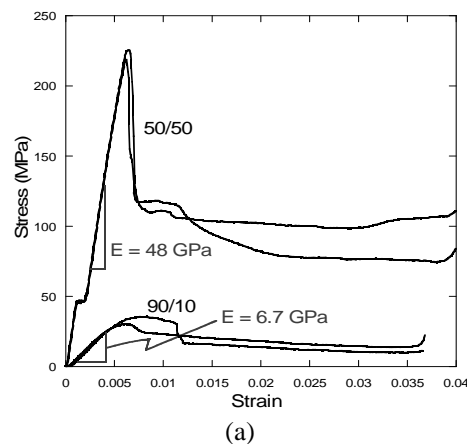


Figure 8. (a) Three-point bend results for two different battery composites. (b) Modes of failure for 50/50 battery composites.

The basic mechanical properties of the battery composites were characterized by performing a basic three point bend test. A span of 5.08 cm and a loading rate of 5 mm/min were used for the mechanical characterization. Figure 8 illustrates the results for two composite battery materials. Both composites use identical processing and reinforcement, as described in Section 4.1, but employ different polymer electrolytes, both solvent-free. The "50/50" curve was generated for a composite whose polymer electrolyte is composed of 50 vol% PEG methyl ether acrylate and 50% PEG(660)₂ bisphenol-A dimethacrylate, while the "90/10" curve was measured for a composite with a polymer electrolyte composed of these two species at 90% and 10%, relatively. Both composites showed reasonable stiffnesses, between 5-50 GPa. The more compliant 90/10 composite demonstrates a lower stiffness, and a more graceful failure. Figure 8b illustrates that under this bending loading condition, failure was dominated by interply failure and fiber buckling. Both failure modes

are expected for composites with compliant matrices. The interply failure mode also indicates the importance of matrix-reinforcement adhesion. Systematic characterization and enhancement of the interfacial adhesion for cathode-electrolyte and anode-electrolyte pairs is in progress, as well as studies with gel electrolytes.

5. CASE STUDY

Unmanned vehicles is one category of applications in which implementation of structural batteries may yield significant benefit. Unmanned vehicles provide support for the soldier on a variety of missions that are undesirable or impossible for a soldier to attempt. For example, they may provide reconnaissance in a location with suspected enemies, explosives, or traps. Properly designed vehicles can sustain extended reconnaissance missions with minimal visibility. Accordingly, some unmanned vehicles are most effective when they contain a wide array of sensors, most of which require electrical energy, while remaining highly mobile, which also requires significant energy.

Incorporation of energy storage into the vehicle structure to provide power to one or more functions of the system as a whole could reduce the overall mass of the vehicle, improving vehicle mobility as well as the logistical support required to transport the vehicle between locations. An additional benefit may be reduction in wiring if individual sensors may be powered directly by the structures to which they are adjacent. An unmanned ground vehicle (UGV), the Lynchbot, is reviewed here for potential mass benefits that the implementation of structural batteries might enable. Specifications have been compiled in order to compare the properties of current and multifunctional platforms.

The Lynchbot is a rectangular vehicle that is approximately 1 m long with an overall mass of 9 kg. The vehicle frame, which supports all wheels, motors, sensors and other attachments, is encased by plastic body panels which we shall refer to as the housing. The housing is not a load-bearing member but simply an outer package to prevent damage to the main inner vehicle components. The minimal structural requirements make the housing an ideal target for replacement with a structural battery, since there is more flexibility with regard to electrolyte matrix formulation. The area of the plastic housing is approximately 1.1 m², including the roof and bottom, with a thickness of 1 mm. The total mass of the housing will depend on the type of plastic; for high strength polycarbonate it will be about 1.4 kg. The vehicle is powered by two military block batteries with energy availability of 20Ah at 15V. The practical energy demand of the UGV is currently 16Ah at 12V. Total battery mass and volume are 3.0 kg and 880

cm³, respectively. In this example the battery mass is over twice that of the housing but the battery volume is only 80% of that of the housing.

The current structural battery design consists of a woven T300 graphite fiber-based anode that is sandwiched between two lithium iron phosphate cathodes, yielding two stacked cells with a nominal open circuit voltage of 3.6V per cell. The components are adhered together using a resin-based structural gel-type electrolyte. Hermetically sealed laminate foil provides environmental protection. A cell in this configuration is typically about 1mm thick, equivalent to the housing thickness. The mass varies according to formulation, but a median areal mass for the above described configuration is 0.22 g/cm², which is 2.4 kg for 1.1 m².

Since the structural battery chemistry has a nominal open circuit voltage of 3.6V, four cells connected in series are required to achieve a replacement voltage of 14.4V. This requirement on the circuit reduces the available amperage by a factor of four – equivalent to a 14.4V battery with an area of 0.275 m² if the entire housing is replaced. The areal energy density in the structural battery is limited by the areal energy density of the anode fabric, since the cathode films may be of variable thickness. Using T300 carbon fabrics, the total areal energy density of the structural battery at 14.4V is expected to have an upper range of 8.0 Ah. In effect, one of the battery packs may be eliminated. The total impact on the system would be a loss of 1.5 kg (for the battery) and a gain of 1 kg (for the added mass in the multifunctional housing) – for a system mass savings of at least 5.5%. Use of a multifunctional battery that has ideal mass efficiency with regard to energy storage and structure would result in no added mass, driving the system-wide mass savings in excess of 16%.

In an alternate scenario, both military batteries would be retained and the multifunctional battery housing would allow for extended mission time and/or additional electronics support without the need to add a third block battery. If the additional electronics only require a device with a nominal voltage of 3.6V, the circuit may be reconfigured to provide 32 Ah. It should be noted that these calculations are all approximate and may be influenced by the need for additional battery protection as well as improvements in design and materials of multifunctional batteries. In addition, power is not evaluated in this example. The structural batteries are expected to have lower power than commercial batteries; however, this may be compensated by the development of hybrid devices that include higher power structural supercapacitors as described in section 4.2.

6. CONCLUSIONS

In summary, we have successfully fabricated and tested multifunctional composite batteries and supercapacitors employing structural polymer electrolytes binding together layers of electrochemically active material. Each of the components in the composite device is itself a multifunctional material. This design concept potentially allows for greater overall mass and/or volume efficiency in any Army platform that utilizes both structural components and energy storage devices.

Towards development and optimization of these high performance structural batteries, our research program is investigating structural resin-based electrolytes, structural carbon anodes, structural cathodes; and integration of these components using scalable composite processing methods. The resin electrolytes allow for a wide range of tailorable properties that are further optimized through the combined use of liquid electrolytes and inorganic nanofillers. Carbon fiber anodes demonstrate sufficient energy storage and are particularly attractive for their compatibility with VARTM processing and the wide range of readily available thicknesses allowing for facile changes in specific loading. The cathodes demonstrate excellent electrochemical capacities and new substrates and film compositions are under investigation. The anodes and cathodes described here are particularly attractive for stacked systems owing to the symmetrical electrochemical activity on both faces. A case study using one such stack was reviewed here with respect to UGVs. Overall, our results indicate that multifunctional structural materials can be realized through the focused development of new materials, material architectures, and low cost scalable fabrication routes. Further quantification of mechanical and electrochemical behavior of the battery composite is required to fully demonstrate the potential of this technology.

ACKNOWLEDGMENTS

We wish to thank Emma Wong for her assistance with testing the carbon fibers anodes; Brian Capaldo for his assistance with the cathodes; Phuong Nguyen for her assistance with gel electrolytes; and Dan Mattson for his assistance with the supercapacitors.

7. REFERENCES

- Ferrari, A.; Robertson, J., 2000: Interpretation of Raman Spectra of Disordered and Amorphous Carbon in *Phys. Rev. B*, **61**, 14095-14107.
- Fong, R.; von Sacken, U.; and Dahn, J. R., 1990: Studies of Lithium Intercalation into Carbons Using Nonaqueous Electrochemical-Cells in *J. Electrochem. Soc.*, **137**, 2009-2013.
- Iijima, T.; Suzuki, K.; Matsuda, Y. 1995: Electronic Characteristics of Various Carbon Materials for Lithium Rechargeable Batteries, in *Synth. Met.*, **73**, 9-20.
- Qian, H; Bismarck, A; Greenhalgh, E; Kalinka, G; Shaffer, M. 2008: Hierarchical composites reinforced with carbon nanotube grafted fibers: The potential assessed at the single fiber level in *Chem. Mater.* **20**, 1862-1869
- Qidwai, M.A.; Baucom, J.N.; Thomas, J.P.; Horner, D.M., 2005: Multifunctional Applications of Thin Film Li Polymer Battery Cells in *Materials Science Forum*, **492-493**, 157-162.
- Snyder, J.; Carter, R.; Wong, E.; Nguyen, P.; Xu, K.; Ngo, E.; Wetzel, E. 2006: Multifunctional Structural Composite Batteries in *Proceedings of SAMPE 2006 Symposium and Exhibition*, Dallas, TX
- Snyder, J.; Carter, R.; Wetzel, E. 2007: Electrochemical and Mechanical Behavior in Mechanically Robust Solid Polymer Electrolytes for use in Multifunctional Structural Batteries in *Chem. Mater.* **19**, 3793-3801.
- Snyder, J.; Wong, E.; Hubbard, C.: Evaluation of Commercially Available Carbon Fibers, Fabrics, and Papers for Potential Use in Multifunctional Battery Applications, *submitted to J. Electrochem. Soc.*
- Takami, N.; Sekino, M.; Ohsaki, T.; Kanda, M.; Yamamoto, M., 2001: New Thin Lithium-Ion Batteries Using a Liquid Electrolyte With Thermal Stability *J. Power Sources*, **97-98**, 677-680.
- Thomas, J. P. and Qidwai, M. A., 2004: Mechanical Design and Performance of Composite Multifunctional Materials in *Acta Materialia*, **52**, 2155-2164.
- Wong, E.; Snyder, J.; Hubbard, C. 2008: Electrochemical Capacities of Commercially Available Structural Carbon Fibers, Fabrics, and Papers in *ARL-TR-4574*.
- Xu, K., 2004: Nonaqueous Liquid Electrolytes For Lithium-Based Rechargeable Batteries in *Chem. Rev.*, **104**, 4303-4417